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OF COMPLEX OR LARGE QUANTITIES OF SAMPLES

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A MASS SPECTROMETER-SPECTRUM DIGITIZER SYSTEM FOR THE ANALYSES

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INTRODUCTION

The system to be described has been established to provide both a wider application and maximum utilization of Langley Research Center gas analysis facilities.

The Langley Vacuum Measurements Section has two functions in the gas analysis field. The first is to develop and to support the development of mass spectrometer ion sources and detectors for special applications. The second is to provide gas analysis services to the many Langley aerospace test facilities, such as high-speed tunnels, vacuum chambers, and life support facilities with an established criteria of 60% R&D, and 40% service. The increased activity in the latter function has resulted in significant delays in both areas, due primarily to the acute shortage of trained personnel. In order to even approach work schedules, it became apparent that a rapid method of obtaining and handling data of a routine nature be devised. The following criteria were established for the system:

1. It should be able to process samples with a minimum of delay.
2. There should be a means of quickly recording a large number of samples for later computer processing, over a range of approximately 0.1% to 100% concentrations.
3. There should be a means of real time data display for checking the system or obtaining an immediate answer.
4. It must be compatible with Langley computing facilities.
5. It should not be so complex as to prevent operation by a trained technician who was not an analyst.

However, a survey of then available equipment indicated that an overall system that would relieve the problem did not exist.

EQUIPMENT

The system now being tested consists of a CEC 21-104 5", 180° spectrometer with a 150° C inlet system and electrometer detector. Useful sample range of the spectrometer will be increased through the addition of a 350° C inlet, direct introduction inlet, and electron multiplier detector. Some electronic modification of the instrument was necessary to mate it with the digitizer, but it is primarily as supplied by CEC.

The mass spectrum digitizer was developed and constructed to Langley specifications by Monsanto Systems Division of St. Louis as a subcontractor to CEC, and provides magnetic tape as well as printed paper tape data recording.

The physical layout of the digitizer is shown in Figure 1. The magnetic tape unit located near the top is a Delta Corder Model TT-L. Immediately below is a Franklin Series B1000 High Speed Printer, a Preston Model 20100 A to D Converter with four digit display; Preston Model 12095 Floating Differential Amplifiers, and Monsanto developed logic, storage converter, and control units. Contained in the control unit is a function switch which selects scan operate (or auto), ion or accel voltage display only on the A/D, and manual input of eight digits per line for identification of runs and to supply certain information required by the computer program.

A much simplified block diagram of the digitizer is shown in Figure 2. The ion and acceleration output voltages from the mass spectrometer are fed through separate floating differential amplifiers and through a switching circuit (not shown here) into the A/D converter. The ion voltage is continuously monitored by the logic unit. This unit samples the incoming signal at a rate of 60 cps, and compares this measurement to the

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previous one which is held in the storage converter. As a peak begins to appear above the baseline "one greater than" followed by "four greater than" or "equal to" signals will command the system to successively replace the lower with higher voltages in the storage converter. As the top of the peak is reached and starts to decay, sensing of "one less than" followed by "four less than" or "equal to" signals will command the system to digitize and store the acceleration voltage. The following command is for the A/D to return to monitoring the ion voltage; and the ion and acceleration data is printed. Output may be recorded in several modes; magnetic tape only, printed tape only, magnetic and printed tape simultaneously, or no record. Although the response of the recorders is extremely fast, the number of steps required to perform the above as presently set up limits the recording rate to two data lines per second, which of course determines the fastest usable scan speed of the mass spectrometer.

Figure 3 shows the manner in which the data is displayed on the paper tape. The first numeral in each column is an attenuation factor. The "A" and "I" indicate ion or acceleration voltage, and the last four digits in the columns are the values of each. The same data is simultaneously placed on the magnetic tape in Binary Coded Decimal.

TESTING AND DATA REDUCTION

The main computation program used is the stepwise regression developed by Tunnicliff and Wadsworth as previously reported in the literature, modified by Tunnicliff for the IBM 7094 computers in use at Langley. The approach is much the same as is often used in computation with a desk calculator - that is, all of the largest peak present in a spectrum is assumed to be contributed to by a single element or compound, and the spectrum is reduced according to its calibration cracking pattern. The residuals are then used to determine the error in the assumption. If the error is greater than a preselected value - normally 1 or 2% - then a second element is forced to enter the regression, and the original calculations adjusted accordingly. This is repeated until the specified residual error is reached, at which time the regression is terminated and the data tabulated. The program consists of three parts: a library tape upon which is stored the cracking patterns of up to 500 elements, with each assigned a unique serial number; a calibration tape to which is transferred from the library tape up to 100 elements to be considered in a particular regression sequence; and the regression part of the program itself. Since the program at present requires card input rather than magnetic tape, it was necessary to write two additional programs to transfer the data from the digitizer tape to cards in a compatible form. These programs are now being combined into one.

Most of the work to date has been the correction of the inequities between the spectrometer and digitizer. For example, noise levels in the spectrometer that are small enough to cause no problem in oscillographic recording are recorded as peaks on the digitizer. Noise level in the system has been reduced to below 1 mV.

To demonstrate the performance realized so far, two known mixtures were made, using a Wallace and Tiernan three turn dial gage as the pressure measuring device. The mixtures were calculated both by hand and by the computer.

The spectrum represented in Figure 4 consisted of CO₂, N₂, O₂, N-Butane, Methane, Ethane, Propane, Freon 12 and Freon 13. The mixture was entered eight times over a period of $1\frac{1}{2}$ hours to simulate multiple samples. It was also considered to be a test of the ability to aid in the reduction of complex samples.

The results obtained are tabulated in Figure 5 and show both operator and computer calculations. The agreement here was very good and may be partly influenced by the fact that the gases making up the mixture were the same ones used in the calibration. However, the potential of the approach has clearly been demonstrated. Total computation time was less than $2\frac{1}{2}$ minutes.

A second mixture was blended to test for analysis of two samples with similar cracking patterns, in this case trans and cis-2 butene. Here we again see the results (Fig. 6) were good, at least close enough to aid in deducing the mixture. The difference here may be caused by the loss of significant figures when entering the data.

The accuracy of the system is calculated to be better than 1% for significant mass peaks. The spectrometer itself is $\pm 0.5\%$ full scale, while the digitizer is $0.01\% + 1$ digit. Precision is found to be about 1 digit.

CONCLUSION

To conclude, a system providing both a latitude in recording modes and with a proven ability to handle both a multiplicity of routine samples and samples of analytical complexity has been devised and placed in service. The prime results of this development are the maximum use of an expensive instrument, preservation of the function goals desired, and elimination of the necessity of instrument and personnel duplication. The present system is not primarily intended for very high resolution, however the improvement of this parameter by the electron multiplier and by increasing the signal sampling rate will be the subject of a later study.

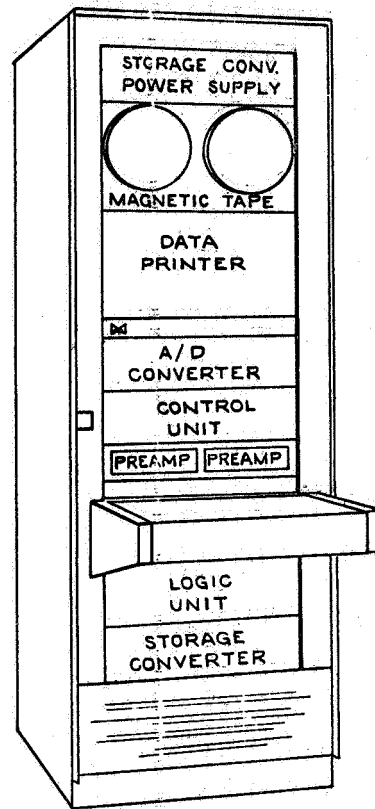


Figure 1

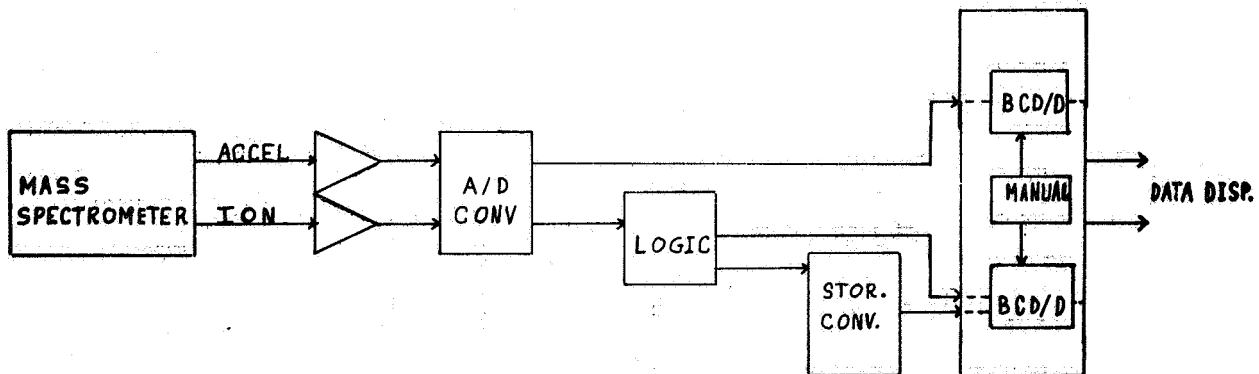


Figure 2

1A0443	110013
1A0515	110053
1A0525	110169
1A0647	110219
1A0679	110006
1A0771	110051
1A0785	110013
1A0813	110004
1A0877	110005
1A0895	110045
1A0953	110005
1A1017	110387
1A1037	110587
1A1063	110079
1A1091	110185
1A1119	110021
1A1144	110091
1A1209	110021
1A1279	110029
1A1397	110101
1A1445	110027
1A1489	110108
1A1539	110596

Figure 3

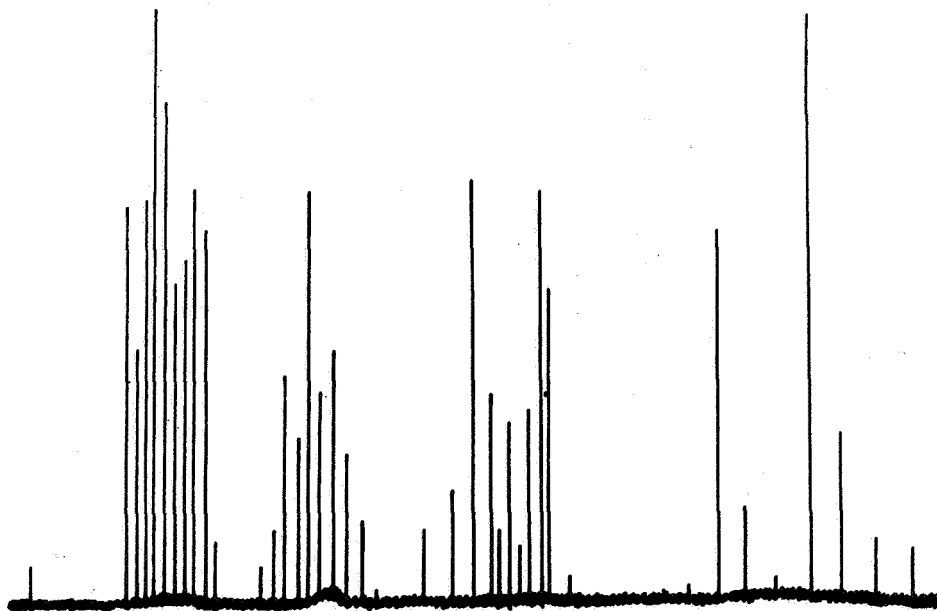


Figure 4

<u>Compound</u>	<u>Operator Calculation (%)</u>	<u>Computer Calculation (%)</u>
Carbon Dioxide CO ₂	9.51	9.50
Nitrogen N ₂	24.20	24.20
Oxygen O ₂	3.31	3.35
N-Butane C ₄ H ₁₀	13.01	13.00
Methane CH ₄	12.20	12.15
Ethane C ₂ H ₆	9.78	9.75
Propane C ₃ H ₈	7.75	7.73
Freon 12 C Cl ₂ F ₂	9.84	9.85
Freon 13 C Cl F ₃	10.38	10.35
Total	99.98	99.78

Figure 5

<u>Compound</u>	<u>Operator Calculation (%)</u>	<u>Computer Calculation (%)</u>
trans 2 Butene	37.79	36.5
cis 2 Butene	62.21	62.4
Total	100.00	98.9

Figure 6